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DETECTION OF METALLIC MORDANTS ON TEXTILES BY PARTICLE-INDUCED X-RAY EMISSION

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Abstract

A group of modern wool and cotton samples prepared as mordanted standards was subjected to particle-induced x-ray emission analysis (PIXE). The mordants applied were potassium aluminum sulfate, cupric sulfate, ferrous sulfate, stannous chloride, and potassium dichromate. Results agreed with analyses of identical mordanted standards by energy-dispersive x-ray spectrometry in a scanning electron microscope (SEM-EDS).

Key Words: Particle-induced x-ray emission, x-ray, mordants, textiles, metal analysis , cotton, wool.

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Introduction

A series of studies performed in the Objects Conservation Department of the Metropolitan Museum of Art, New York, has suggested that energy-dispersive x-ray spectrometry with a scanning-electron microscope (SEM-EDS), serves well for the analysis of metallic mordants on textiles (Koestler et al., 1985a); (Indictor et al., 1985); (Koestler et al., 1985b). The analytical procedure applies also to metal-wrapped yarns (Indictor and Koestler, 1986), metallic salts used to weight fabrics (Ballard et al., 1985), pigments painted on textile (Lee-Whitman and Skelton, 1983), and special dyes which contain elements above fluorine (e.g., shellfish purple, 6,6'dibromoindigo, also known as Tyrian Purple)(Koestler et al., 1985a). In addition, the analysis may be used to characterize accretions on the surface of a textile, indicating evidence for the history of the artifact (Koestler et al., 1985b). If the accretion contains substances with elements heavier than fluorine, these elements will be detected. Substances containing elements lighter than fluorine escape detection. Hence, most organic dyes escape detection; organic mordants or additives (e.g., sumac, tannins, fatty acids, etc.) also escape detection (Indictor et al., 1985).

An alternative analytical procedure, particle-induced x-ray emission (PIXE), is capable of producing the same data with comparable sensitivity and limitations. To test the appropriateness of this analytical procedure, a group of mordanted cotton and wool samples prepared in the Textile Conservation Laboratory of the Metropolitan Museum were subjected to PIXE analysis. The samples were taken from the same fabrics already assayed by SEM-EDS. The results were comparable in each case. The PIXE system can detect the presence of aluminum, but magnesium is difficult because of absorption of the soft x-ray in the detector window. Sodium is not detectable.

Experimental

Materials: Samples of wool and cotton fabric were prepared by the Metropolitan Museum Textile Conservation Laboratory as references for mordant analysis. Mordanting procedures have been described (Koestler et al., 1985a). The mordants used were: potassium aluminum sulfate (alum), $K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$; cupric sulfate, $CuSO_4 \cdot 5H_2O$; ferrous sulfate, $FeSO_4 \cdot 7H_2O$; stannous chloride, $SnCl_2 \cdot 2H_2O$; potassium dichromate, $K_2Cr_2O_7$.

PIXE Analysis: Samples were prepared by affixing one fiber from each sample to a 6.4 μm thick polypropylene film by means of one drop of a 2.5% (wt) solution of polystyrene in toluene. No further sample preparation was necessary except to mount the film on a 35 mm slide card. The targets so prepared were placed in a modified Kodak Carousel projector which served as an 80-slide sample changer and were subjected to a 100 nanoamp beam of 2 MeV protons in an atmosphere of helium. An energy-dispersive Si(Li) detector was used to obtain the x-ray spectra. The external-beam PIXE system at Brooklyn College has been described elsewhere in detail (Williams et al., 1981) (Bauman et al., 1979). Analysis of each sample required less than five minutes. Samples can easily be stored for later reanalysis if desired, since the analysis is nondestructive. Samples are not coated as is required in SEM analysis. A representative spectrum is shown in figure 1.

Results and Discussion

Analysis of the cotton samples showed clearly the metallic mordants expected in each case. No evidence of these metals was seen in the untreated cotton. A trace of iron and occasionally small amounts of zinc and copper were seen in all spectra due to background in the sample chamber. This background was negligible compared to the metallic mordants but did set a limit on the ultimate sensitivity for these elements.

Similarly, PIXE analysis of the wool samples detected the presence of the expected metallic mordants in the standard samples. A major difference in this sample set was the common presence of a sulfur peak, absent in cotton, as expected, and prominent in wool due to the cystein and methionine links in the proteinaceous substrate (Stephens, 1975). The clear sulfur x-ray peak in PIXE analysis of wool (and presumably silk) may provide an internal standard for possible quantitative mordant determination (and in any case, easy relative comparisons) as pointed out for SEM-EDS analysis of dyed wool samples (Indictor et al., 1985) and historical silks (Koestler et al., 1985a, 1985b).

Quantitative mordant assay is possible with PIXE by comparing the x-ray peak intensities in the spectrum of the sample with those obtained by bombarding reference samples of known concentrations. The accuracy of the analysis is less for the lightest elements because of absorption of the soft x-rays in the fibers themselves and in the Si(Li) detector window. This problem is important for aluminum and sulfur but much less so for elements of higher atomic number. Sample self-absorption of soft x-rays occurs regardless of whether SEM-EDS or PIXE is used. Thus, absolute analysis is difficult by any energy-dispersive method.

Small portions of the reference samples have been subjected to analysis by atomic absorption (Koestler et al., 1985a) (Indictor et al., 1985). The results of such analysis could be used to calibrate the PIXE system. In principle, it is necessary to calibrate all quantitative results of this type with an independent method of analysis because a major portion of the sample (elements of atomic number < 13) escapes detection. Effects of sample self-absorption etc., would then be accounted for assuming that other fibers subject to analysis have roughly the same physical characteristics.

In evaluating PIXE or SEM-EDS methods of analysis, the question of surface versus bulk inclusion of mordants in the fibers in the analytical process arises. The penetrating range of protons or electrons in matter is a function of particle energy, mass, and charge as well as density and atomic mass of the material traversed. A textile fiber is a rather open material and exact calculation of the penetration depth of particles is difficult. The linear range of a 2 MeV proton in solid carbon is about 0.1 mm. A 2 MeV proton has roughly the same penetrating power as a 100-keV electron so that SEM-EDS systems employing such electrons have comparable penetration of the bulk of the samples.

The chief advantage of PIXE analysis over SEM-EDS is the ultimate sensitivity which can be achieved with the former technique. Sensitivity is limited in SEM-EDS by the large contribution to the background due to electron bremsstrahlung. The overall intensity of bremsstrahlung background in PIXE is about one hundred times less with a corresponding increase in sensitivity compared to SEM-EDS. For example, it is readily possible to detect the presence of 20 ng of chromium or iron in a 1 mg fiber which yields a sensitivity of 20 ppm.

Comparing our results with those of (Koestler, et al., 1985a) we note that in the case of wool samples mordanted with Fe, Sn, and Cr, a single fiber was insufficient for SEM-EDS analysis but was sufficient for PIXE. In fact, figure 1 represents the PIXE spectrum for a single fiber of wool mordanted with Fe.

Conclusions

Modern samples of cotton and wool mordanted with potassium aluminum sulfate, ferrous sulfate, cupric sulfate, stannous chloride, and potassium dichromate were analysed successfully for Al, Fe, Cu, Sn, and Cr by

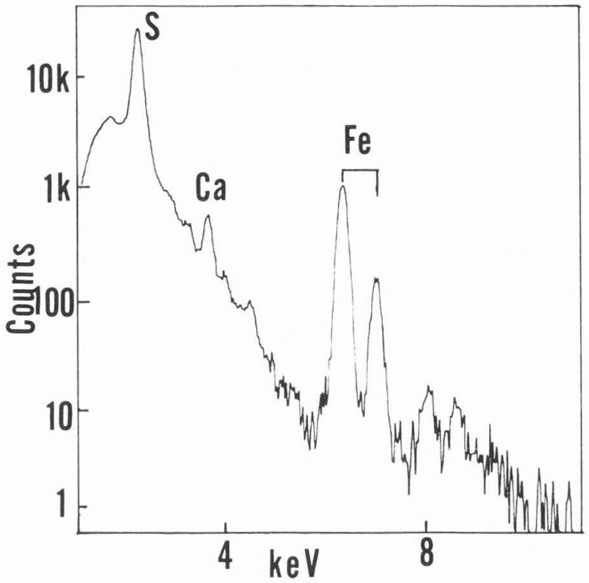

Fig. 1. PIXE spectrum of single wool fiber mordanted with Fe.

PIXE. The persistent observation of trace metals even for samples not treated with mordant indicates the importance of background scans for these analyses. The clear presence of sulfur in PIXE analysis of wool suggests the possibility of its use as an internal standard in quantitative estimates of metallic mordants or related material on proteinaceous fibers.

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Discussion With Reviewers

H. Blank: It would help the reader if the authors would differentiate between the techniques which produce the electron-shell vacancies (i.e., protons for PIXE and electrons in an electron microscope) and the energy-dispersive spectrometer (EDS) which is used in both cases for the analysis of the x-rays.
Authors: We agree. The term EDS has been often used in the world of scanning electron microscopists. As EDS is also used in PIXE and x-ray fluorescence, it is clear that a new acronym is needed. Since electron-induced x-ray emission does not yield a "good" acronym (EIXE) we have decided, for the purpose of clarity in this paper, to use SEM-EDS to denote energy-dispersive x-ray spectrometry in a scanning electron microscope (instead of EDS).

H. Blank: Did you find inhomogeneity in your samples, and could you observe beam damage of your samples with PIXE? What accuracy do you expect from PIXE analysis?
Authors: The fiber samples were about 1 mm diameter by 3 mm long. The beam spot had a 1 cm diameter so that the result referred to the entire fiber. No beam damage was observed. The He atmosphere allows for cooling of the sample. Quantitative analysis by PIXE is generally accurate to 5-10 percent on a routine basis with better accuracy possible if stringent precautions are taken.

Reviewer III: What are the comparative advantages of PIXE (in the case of analyzing textile fibers) over x-ray fluorescence (XRF) as well as SEM-EDS?
Authors: The chief advantage of PIXE over XRF for textile fiber analysis is that a single fiber is too small for conventional XRF but not for PIXE.

J.R. Chen: What was the range of sulfur concentrations in the wool samples and would large variations negate the use of sulfur as an internal standard?
Authors: Inasmuch as this was a feasibility study, qualitative rather than quantitative analysis was performed. The fibers were not weighed. There did not appear to be large variations in sulfur content in the six wool samples analyzed. Use of sulfur as an internal standard, however, is not yet established as it is known that sulfur can be lost as the fibers age and the sulfur content may change depending on how the textile is handled over the course of time. Further research would be required.

H. Blank: A wavelength-dispersive spectrometer is more sensitive due to better peak-to-background ratio. Did you carry out investigations of your samples with an electron microprobe?
Authors: No, we did not use wavelength-dispersive analysis.